

Controlling the Local Spin-Polarization at the Organic-Ferromagnetic Interface

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By means of *ab initio* calculations and spin-polarized scanning tunneling microscopy experiments we show how to manipulate the local spin-polarization of a ferromagnetic surface by creating a complex energy dependent magnetic structure. We demonstrate this novel effect by adsorbing organic molecules containing $\pi(p_z)$ -electrons onto a ferromagnetic surface, in which the hybridization of the out-of-plane p_z atomic type orbitals with the d -states of the metal leads to the inversion of the spin-polarization at the organic site due to a $p_z - d$ Zener exchange type mechanism. As a key result, we demonstrate that it is possible to selectively inject spin-up and spin-down electrons from the same ferromagnetic surface, an effect which can be exploited in future spintronic devices.

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Combining molecular electronics with spintronics represents one of the most exciting avenues in building future nanoelectronic devices [1–3]. For example, widely used in spintronic applications, the spin valve [4] is a layered structure of two ferromagnetic electrodes separated by a nonmagnetic spacer to decouple the two electrodes and allows spin-polarized electrons to travel through it. The efficiency of a spin valve depends crucially on the spin injection into and spin transport throughout the non-magnetic spacer. On one side, since organic molecules are made of light elements with weak spin-orbit coupling as C and H, their use as spacer materials is very promising for transport properties since the spin coherence over time and distance is much larger than in the conventional semiconductors present in today's devices [5–7]. On the other side, the spin injection is mostly controlled by the ferromagnetic-organic layer interface [8, 9] which is responsible for the significant spin loss in devices [10]. Therefore, a large effort is made to control the electronic properties at the organic-magnetic interfaces and, in this context, the theoretical first-principles calculations represent an indispensable tool to understand and guide experiments toward more efficient devices.

In this Letter we propose a simple way to manipulate the local spin-polarization of a ferromagnetic surface by flat adsorbing organic molecules containing $\pi(p_z)$ -electrons onto it. As a consequence, around the Fermi level an inversion of the local spin-polarization at the organic site occurs with respect to the ferromagnetic surface due to a complex energy- and spin-dependent electronic structure of the organic-metal interface. The interaction between the molecule and the ferromagnetic surface reveals a mechanism similar to the $p_z - d$ Zener exchange [11] and enables a selective control of electron injection with different spins [i.e. up(\uparrow) or down(\downarrow)] from the same ferromagnetic surface within a specific energy

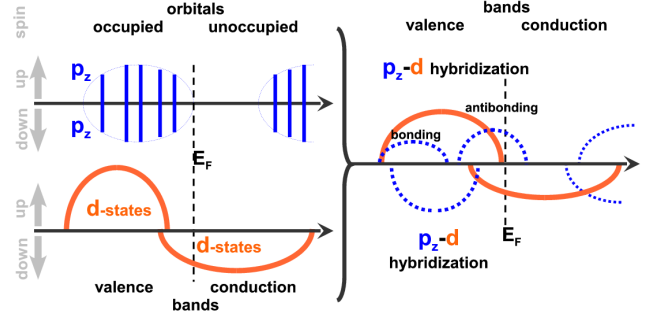


FIG. 1: (Color online) A $p_z - d$ Zener exchange type mechanism explains the interaction between nonmagnetic organic molecules with a ferromagnetic surface. (left) Cartoons of the molecular electronic structure (upper panel) and the density-of-states of the ferromagnetic surface (lower panel). (right) The p_z atomic orbitals in the spin-up channel hybridize with the majority (spin-up) states of the Fe atoms forming bonding (at lower energies) and antibonding (at higher energies) states some of them being pushed above the Fermi level. Due to the $p_z - d$ interaction in the spin-up channel, the spin-down states are lowered in energy and slightly hybridize with the minority states of Fe. As a consequence, for a given energy interval the number of spin-up states is different than the number of spin-down states.

range near the Fermi level.

In a first step, we performed *ab initio* calculations of benzene (Bz), cyclopentadienyl radical (Cp) and cyclooctatetraene (Cot) molecules adsorbed on a ferromagnetic 2ML Fe/W(110) surface, a prototypical system used in spin-polarized scanning-tunneling microscopy (SP-STM) experiments [12]. The choice of the calculated molecule-ferromagnetic surface systems can be understood as following: (i) although having a low reactivity, Bz (C_6H_6) is an aromatic 6π -electron system [13] that can form sandwich type compounds with d -metals [14] and chemisorbs

on reactive surfaces [15, 16]; (ii) a high-reactive 5π -electron system, Cp (C_5H_5) strongly interacts with d -metals and forms an aromatic 6π -electron system in sandwich type molecules like ferrocene [13]. However, Cp can be brought on the surface by decomposition of the ferrocene molecule which occurs after its adsorption on metallic surfaces [17]; (iii) an 8π -electron system, Cot (C_8H_8), binds strongly the metal atoms by forming an aromatic 10π -electron system [13] and is well known to react even with f -electrons of rare earth metals [18, 19] forming sandwich type molecules and long nanowires [20].

In a second step, to confirm theoretical predictions as well as the generality and broad applicability of the $p_z - d$ Zener exchange type mechanism, we performed spin-polarized scanning tunneling microscopy experiments [21, 22] for a phthalocyanine molecule (H_2Pc) adsorbed on 2ML Fe/W(110). The choice of the H_2Pc ($C_{32}N_8H_{18}$), an $40\pi(p_z)$ -electron system, is motivated by its flat structure and the large size which makes it an easy observable in experiments [21, 23].

Our spin-polarized first-principles calculations are carried out in the framework of density functional theory (DFT) by employing the generalized gradient approximation (PBE) [27] in a projector augmented plane-wave formulation [24] as implemented in the VASP code [25, 26]. The molecule-Fe/W(110) system is modeled within the supercell approach [p(5×3) in-plane surface unit cell] and contains five atomic layers (3 W and 2 Fe) with the adsorbed molecule on one side of the slab [28]. Using a plane-wave energy cutoff of 500 eV in our *ab initio* calculations, the uppermost two Fe layers and the molecule atoms were allowed to relax until the atomic forces are lower than 0.001 eV/Å. As a general characteristic of the geometric structure, we note that all molecules like to bind with the C and/or two C atoms on top of Fe surface atoms so that the shortest C–Fe bond is about 2.2 Å. Furthermore, each of the molecules is nonmagnetic [29] upon adsorption on the ferromagnetic surface.

We will first conceptually discuss the mechanism present at the molecule-metal interface as schematically depicted in Fig. 1. The general mechanism, also known as $p_z - d$ Zener exchange mechanism, is commonly used to explain how a magnetic impurity in a semiconductor host remains magnetic [30] where, due to the $p - d$ mixing, the p -band of the semiconductor is broadened and part of it is pushed above the Fermi level (often referred as the hole which is created in the p -band). In our specific case, the nonmagnetic molecule represents the impurity and its orbitals become spin-split after the interaction with the d -states of the ferromagnetic surface occurred. As shown in Fig. 1, in the spin-up channel the p_z atomic type orbitals which originally form the π -molecular orbitals hybridize with the majority d -states of the Fe atoms forming molecule-metal hybrid states with bonding and antibonding character. The bonding states are situated at low energies while the antibonding states

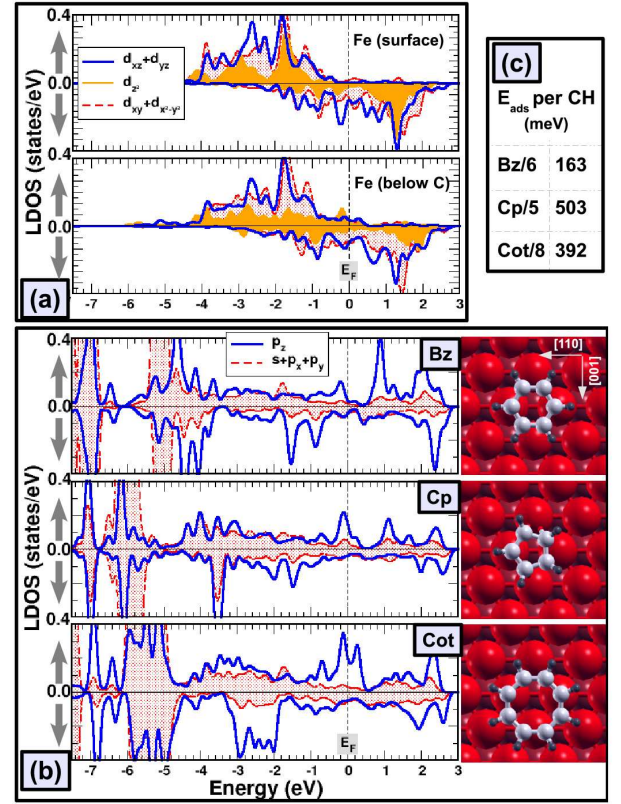


FIG. 2: (Color online) (a) Spin-resolved local density-of-states of an Fe atom of the clean surface (upper panel) and an Fe atom below C atom of the Cot molecule (lower panel); (b) adsorption geometries and the spin-resolved local density-of-states of the Bz, Cp and Cot molecules adsorbed on the 2ML Fe/W(110); (c) the adsorption energies of the Bz (C_6H_6), Cp (C_5H_5) and Cot (C_8H_8) are given in meV per CH group of atoms. Compared to Bz, Cp and Cot molecules interact strongly with the surface due to an effective hybridization between out-of-plane orbitals (p_z of C and d_{z^2} , d_{xz} , d_{yz} of Fe), while the in-plane orbitals are weakly interacting (s , p_x , p_y of C and/or $d_{x^2+y^2}$, d_{xy} of Fe). All adsorbed molecules show a general characteristic: the *energy dependent spin-polarization*, i.e. in a given energy interval the number of spin-up and spin-down electrons is *unbalanced*. For this specific interval the molecule has a net *magnetic moment* delocalized over the molecular plane, although the total magnetic moment of the molecule is 0.0 μ_B . Note also the larger weight of the states crossing the Fermi level situated in the spin-down channel at metal site and in the spin-up channel at molecular site.

appear at much higher energies, more precisely in an energy window situated around the Fermi level. Due to the $p_z - d$ interaction in the spin-up channel, the spin-down p_z atomic type orbitals are lowered in energy and slightly hybridize with the minority d -states of Fe. As a consequence, the states with large weight around the Fermi level are in the spin-down channel at clean metal sites and in the spin-up channel at the molecule site.

The spin-resolved local density-of-states (LDOS) of the

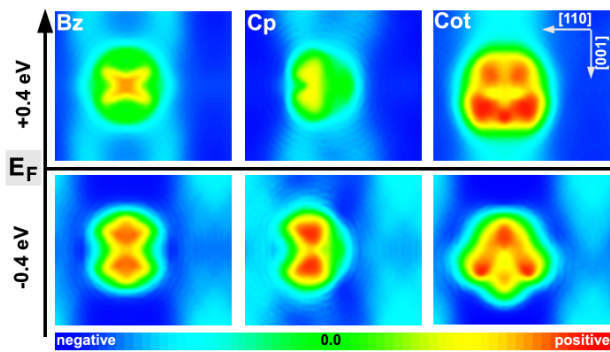


FIG. 3: (Color online) The spin-polarization at 2.5 Å above the Bz, Cp, and Cot molecules adsorbed on 2ML Fe/W(110) ($15.85\text{\AA} \times 13.45\text{\AA}$) surface plotted for occupied $[-0.4, 0.0]$ eV and unoccupied $[0.0, +0.4]$ eV energy intervals around the Fermi level. All the organic molecules show a high, locally varying spin-polarization ranging from attenuation to inversion with respect to the ferromagnetic Fe film. As compared to Bz, the strongly interacting Cp molecule shows an amplification of the inversion of the spin-polarization below Fermi level, while the Cot molecule shows a strong amplification of the inversion of the spin-polarization for both occupied and unoccupied states around the Fermi level due to a higher number of p_z interacting electrons.

molecule-ferromagnetic surface systems clearly illustrate the above described mechanism. In Fig. 2 (a) we plot the LDOS of a clean surface Fe atom (upper panel) and an Fe below a C atom (lower panel). As compared to the clean surface Fe atom, for the Fe below C, the shape of the out-of-plane spin-up d -states (d_{z^2} , d_{xz} , d_{yz}) is strongly changed due to the hybridization with the out-of-plane spin-up p_z atomic orbitals of the C. However, the spin-down d -states of iron and p_z -orbitals of carbon as well as the in-plane states in both spin channels $d_{x^2+y^2}$, d_{xy} of the metal and s , p_x , p_y of the molecule are less affected by the molecule-surface interaction. Characteristic for the strongly interacting molecules as Cp and Cot [Fig. 2 (b)] are the spin-up $p_z - d$ bonding states in the $[-5.0, -3.0]$ eV energy interval and the spin-up antibonding states around the Fermi level in the $[-1, +1]$ eV energy interval. In the spin-down channel the states having high weight at the molecular site are situated at low energies, i.e. $[-3.0, -2.0]$ eV energy interval for Cot molecule and around $[-3.5, -1.5]$ eV energy interval for Cp molecule. Since the Bz-surface interaction is weaker as compared to Cp and Cot molecules [see adsorption energies (E_{ads}) given in Fig. 2 (c)], the spin-up antibonding molecule-surface hybrid states have smaller weight around the Fermi level while the spin-down states at the molecule site are not shifted as low in energy (i.e. $[-2.0, -0.8]$ eV energy interval).

The spin-polarized LDOS of the adsorbed Bz, Cp and Cot molecules show a very interesting feature: the *energy dependent spin-polarization*. As clearly seen in Fig. 2 (b) for a given energy interval the number of spin-up and

spin-down states is *unbalanced*. For that specific interval the molecule has a net *magnetic moment* delocalized over the molecular plane since it is carried mostly by the p_z states. This implies that, in a SP-STM experiment for which the energy interval is selected by the applied bias voltage, the molecule will show a *magnetic contrast* although each of the adsorbed molecule is nonmagnetic [29] upon adsorption on the ferromagnetic surface.

Even more interesting, as depicted in the LDOS, around the Fermi level the states with high weight are in the spin-up channel at the molecular site, while on the clean Fe surface these states are in the spin-down channel. As a consequence, at the molecular site an *inversion* of the spin-polarization [31] occurs with respect to the ferromagnetic surface.

This effect is clearly illustrated in Fig. 3 by the spin-polarization at 2.5 Å above the molecule in the energy intervals below $[-0.4, 0.0]$ eV and above $[0.0, +0.4]$ eV the Fermi level. A common characteristic for all the molecule-ferromagnetic surface systems is the high and locally varying spin-polarization ranging from *attenuation* to *inversion* with respect to the ferromagnetic surface. Since the carbon's p_z atomic orbitals of the Cp and Cot molecules are strongly interacting with the d -states of the iron atoms, as compared to Bz molecule, an *amplification* of the molecule's local spin-polarization below Fermi level occurs. Moreover, because of the higher number of p_z electrons present in Cot molecule, many antibonding $p_z - d$ hybrid states with high weight above the Fermi level are created. Overall, this results in a strong *amplification* of the molecule's local spin-polarization also above the Fermi level (see Fig. 3) as compared to Bz and Cp molecules.

In general, the probability to inject spin-polarized electrons from a ferromagnetic electrode is proportional to the density-of-states near the Fermi level, i.e. with the spin-polarization in the energy interval defined by the applied bias voltage. Our first-principles calculations demonstrate that by flat adsorption of organic molecules onto the ferromagnetic surface, an *inversion* of the spin-polarization occurs with respect to the ferromagnetic iron film. We conclude that it is possible to control locally the injection of electrons with different spins (i.e. up or down) from the same ferromagnetic surface by flat adsorbing organic molecules containing $\pi(p_z)$ -electrons onto it. With other words, from the clean ferromagnetic surface mostly the spin-down (\downarrow) electrons will be injected while locally, at the molecule site, mostly the spin-up (\uparrow) electrons are injected.

To validate the predictions of the *ab initio* calculations and to demonstrate that the mechanism explaining the organic-ferromagnetic metal interface discussed in Fig. 1 is *general* and *widely* applicable for other flat organic molecules which contain $\pi(p_z)$ -electrons, we have performed SP-STM experiments [34] on the large-size phthalocyanine molecule (H_2Pc) adsorbed on

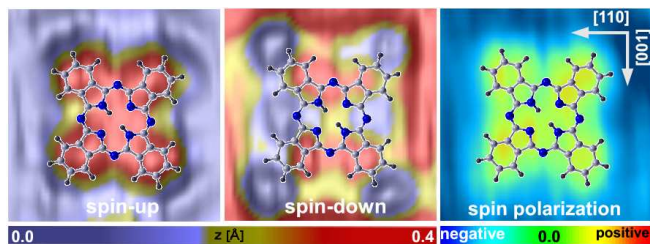


FIG. 4: (Color online) Experimental ($22\text{\AA} \times 22\text{\AA}$) SP-STM images for H_2Pc adsorbed on 2ML Fe/(W110) at $U = +0.05$ V for both spin channels [i.e. up (\uparrow) and down (\downarrow)] and local spin-polarization. H_2Pc molecules show a high, locally varying spin-polarization ranging from attenuation to inversion with respect to the ferromagnetic Fe film.

2ML Fe/(W110). Due to its $\pi(p_z)$ -electrons, the H_2Pc molecule has a flat structure and is well known for its high reactivity similar to the one of the Cot molecule, i.e. H_2Pc reacts with (a) d -metals forming metal-phthalocyanine (MPc) molecules [13] or (b) f -metals yielding sandwich type organometallic compounds [32].

The experimental SP-STM images recorded for the H_2Pc adsorbed on 2ML Fe/(W110) (see Fig. 4) clearly show that the H_2Pc molecule exhibits a magnetic contrast in the $[0.0, 0.05]$ eV energy interval above Fermi level (i.e. the molecular appearance of the spin-up and spin-down channels is obviously different). As a consequence, in this specific energy interval, the H_2Pc molecule has a net magnetic moment delocalized over the molecular plane as depicted in Fig. 4 by the experimentally determined local spin-polarization [33].

To summarize, we have shown that the spin-polarization of a ferromagnetic surface can be locally *inverted* by flat adsorbing organic molecules containing $\pi(p_z)$ -electrons onto it. The complex energy dependent magnetic structure created at the organic molecule-surface interface resembles the p_z-d exchange type mechanism. Although the adsorbed molecules are nonmagnetic, due to an energy dependent spin-polarization, in a given energy interval the molecules have a net magnetic moment delocalized over the molecular plane. Highly electronegative molecules as Cp and Cot strongly interact with the ferromagnetic surface which yields to an amplification of the inversion of the spin-polarization as compared to less reactive molecules as Bz. Moreover, the generality of the theoretical results and the p_z-d exchange type mechanism is further demonstrated by our SP-STM experiments on the H_2Pc adsorbed on the 2ML Fe/(W110) surface which clearly show the inversion of the local spin-polarization near the Fermi level. Our combined first-principles and experimental study demonstrates that electrons of different spin [i.e. up (\uparrow) and down (\downarrow)] can selectively be injected from the same ferromagnetic surface by locally controlling the inversion of the spin-polarization close to the Fermi level, an effect

which can be exploited to increase the efficiency of future molecular spintronic devices.

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- [29] (a) Integrating the spin-resolved LDOS for each molecule yields very small magnetic moments, i.e. $0.076 \mu_B$ for Bz, $0.031 \mu_B$ for Cp and $0.003 \mu_B$ for Cot because of a slightly higher number of electrons in spin-down channel (\downarrow). These magnetic moments can be practically neglected and the adsorbed molecules can be considered non-magnetic (i.e. $0.0 \mu_B$). (b) For a clean surface Fe atom, due to the higher number of electrons in spin-up channel (\uparrow), we find a magnetic moment of $2.834 \mu_B$ as the one reported by Qian *et al.* in *Phys. Rev. B* **60**, 16192 (1999). The magnetic moment of the Fe below C decreases with $\approx 0.4 \mu_B$, i.e. to a value of $\approx 2.4 \mu_B$.
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